UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION VII
901 NORTH 5TH STREET
KANSAS CITY, KANSAS 66101

MEMORANDUM

TO: Bruce Morrison
Project Manager, Herculaneum Lead Smelter Site

FROM: Michael F. Davis
Environmental Scientist

SUBJECT: Document Review: "Final Report, The Speciation and Bioaccessability Of Anomalous Lead Concentrations In Soils From The Herculaneum Community – Herculaneum, Missouri," dtd. May 24, 2005, by Dr. John W. Drexler, Laboratory For Environmental And Geological Studies, University of Colorado, Boulder CO 80309

Per your request, I have reviewed the subject final report. My comments follow:

1. The author uses the terms, "bioavailable" and "bioaccessible" interchangeably in the text, tables, and illustrations of this document. The Quality Assurance Project Plan (QAPP) entitled, "Final Addendum QAPP Site Characterization at the Herculaneum Lead Smelter," dtd. August 2004, contain standard operating procedures (SOPs) from the University of Colorado for both the "In-Vitro Method, Relative Bioavailability Leaching Procedure" and for lead compound speciation by the electron microprobe (EMPA) technique. The only term used in the in-vitro method which refers to the potential for oral uptake of lead bearing compounds is "bioavailability." There is no reference to calculation of either bioavailability or bioacessability in the EMPA speciation SOP. The EPA document, "Short Sheet: IEUBK Model Bioavailabilty Variable" (EPA # 540-F-00-006) contains the following definitions, "As indicated in the Guidance Manual for the IEUBK Model, **bioavailability** refers to "the fraction of the total amount of material in contact with a body portal-of-entry (lung, gut, skin) that enters the blood." Bioavailability is also described as absolute or relative (USEPA, 1994). **Absolute bioavailability** is the amount of a substance entering the blood via a particular route of exposure (*e.g.*, gastrointestinal) divided by the total amount administered (*e.g.*, soil lead ingested). **Relative bioavailability** is indexed by measuring the bioavailability of a particular substance relative to the bioavailability of a standardized reference material, such as soluble lead acetate..."**Bioaccessability**" is a term used in describing an event that relates to the absorption process. It generally refers to the fraction of administered substance that becomes solubilized in the gastrointestinal fluid. For the most part, solubility is a prerequisite of absorption, although small amounts of lead in

A717 9.0

particulate or suspended/emulsified form may be absorbed by pinocytosis. Moreover, it is not simply the **fraction** dissolved that determines bioavailability, but also the **rate** of dissolution, which has physiological and geochemical influences. In and of itself, bioaccessability is not a direct measure of the movement of a substance across a biological membrane (*i.e.*, absorption or bioavailability). The relationship of bioaccessability to bioavailability is ancillary and the former need not be known in order to measure the latter." Recommend that these definitions be adopted throughout the document to clarify the contextual meaning of the data.

2. Page 10, bottom paragraph. Were the vacuum bags used to create a composite sample for the in-vivo study? If so, please state.

3. Page 11, first paragraph. Recommend revising final sentence to read, "The interior house dust vacuum bag samples were prepared for shipment to the University of Missouri....

4. Page 19, delete first three sentences.

5. Page 24, the calculation of "Bioaccessable Mass Lead (Bio_{Pb}) is described in the final report, but is not described in either the University of Colorado SOP for EMPA or the metal speciation SOP attached to this report. The reasoning behind the calculation is presented in the report and the approach appears to be sound as a method to supplement invitro or invivo analysis which captures only the total contribution of all bioavailable lead species. This approach enables the data user to make decisions regarding the prevalent lead bearing species in a sample and their potential for individual relative contribution to lead bioavailability. Caution is advised, however, for the use of this data as there is no statement made regarding the quantitative comparability of this analysis to either invitro or invivo study methods.

6. Pages 60-62, Table 4.10, Residential Soil Speciation. There are numerous instances in this table where the F% (Frequency of Occurrence) for various lead species is reported as a non-numeric, "Trace Value" yet, percent relative masses, and bioaccessable lead concentrations are reported. Please explain.

7. Tables 4.10, Residential Soil Speciation v.s. Table 4.9, Interior Dust Speciation. The percent frequency of occurrence of galena in indoor dust ranges from 63.4% to 8.29% wile the frequency of occurrence in the residential soil samples ranges from non detect through only 0.093%. Roadside samples exhibit a galena frequency of occurrence range from 74.78 to 9.66%. Can the distribution of galena in these samples be explained?

8. Page 81, Speciation Analysis. The SOP from the University of Colorado for EMPA analysis reads as follows, "The precision of the data generated by the "EMPA point count" will be evaluated by calculating RPD values for all major (>20% frequency) phases, comparing the original result with the duplicate result. If the duplicate analyses are from samples that have produced at least 100 total particles it is expected that all (100%) of the dominant species (representing 60% of frequency) be found in both, and

that their individual frequency of occurrence not vary by more than 30%, relative. In the evaluation of the method precision it is most important to consider the variation in results among all samples studied for a particular media, since the overall particle count is very large." Therefore, the relative percent difference between duplicate samples for all major phases in a given matrix should not vary by more than 30%. The data in the final report are presented in graphical format; therefore the numerical values presented below are best estimates from the graphs.

a. For the duplicate analysis from Baghouse 3, there was only one species reported as a major phase (>20% frequency). Pb salt was reported at 92% in the sample and 75% in the duplicate with relative percent difference = 20.4%

b. For the duplicate analysis named "Cool Baghouse", both slag and galena were identified as major phases in at least one sample. Galena was reported at 53% in the sample and 28% in the duplicate with relative percent difference = 61.7%. Slag was reported at 5% in the sample and 32% in the duplicate with relative percent difference = 145.9%

c. For the duplicate analysis named, "Roadside-2",CaFeO and Cerussite were identified as major phases in at least one sample. CaFeO was reported at 21% in the sample and 35% in the duplicate with a relative percent difference of 50%. Cerussite was reported at 26% in the sample and 13% in the duplicate with a relative percent difference of 67%

d. For the duplicate analysis named "306 Main Dust", Galena was the only major phase identified. Galena was reported at 49% in the sample and 47% in the duplicate with a relative percent difference of 4%. It is interesting to note, however, that the reported relative lead mass for 306 Main is higher in the duplicate than the sample.

The author states that all observed variations are considered acceptable, thus no corrective action is required. This statement does not appear to be supported by the data.

The August, 2004 Site Investigation Field Sampling Plan for the Herculaneum Lead Smelter Site (HLS) lists three primary objectives for the project: 1) Determine the sources of lead in residential contaminated soils and interior house dusts surrounding the HLS; 2) Determine the apportionment of lead species in the residential contaminated soils and interior house dust; 3) Determine the bioavailability of lead species found near the smelter. The author broadly concludes that the lead in residential soils in the Herculaneum area are the result of activities associated with the Doe Run operation and include; smelter-stack emissions, fugitive emissions from hauling and storage as well as waste and concentrate spillages. Objectives one and two for this project were generally fulfilled by the EMPA analysis while objective three was fulfilled by the in-vitro relative bioavailability analysis. For the purpose of project objectives one and two, the imprecision in duplicate samples, though outside of published acceptance limits, does not

adversely affect the ability to generally conclude that HLS activities have contributed to soil and dust borne lead concentrations. It is much more difficult, however, to draw conclusions about the specific HLS activity that may be the major contributor to lead contamination in residential soils and interior dusts.

If you have any questions or comments about my review, please contact me by phone at X7096.